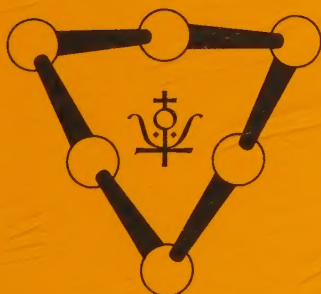


INORGANIC MERCURY(II) COMPOUNDS

A Structural Study of Salts with
Hg-O, Hg-F and Hg-Cl Bonds

CLAES STÅLHANDSKE



Lund 1980

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CLAES STÅLHANDSKE

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Abstract

Structural studies of some inorganic mercury(II) compounds have been carried out with X-ray and neutron diffraction techniques. Building elements of the investigated and some closely related compounds are described. Two-coordination is most common for Hg(II) with oxygen as ligand, but examples of four, six and also eight-coordination are found.

The hydrogen bonds, in the five hydrates investigated by neutron diffraction, are weak or of intermediate strength. The water molecules have all an approximately tetrahedral environment with both hydrogen atoms involved in hydrogen bonds. The hydrates have been thermal investigated by DTA.

A comparison is made between structures of salts of Hg(II) and other cations, especially Cd(II). Coordination numbers and bond lengths in the isomorphous compounds: HgSO_4 , CdSO_4 , $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$, $\text{CdSeO}_4 \cdot \text{H}_2\text{O}$; $\text{HgF}(\text{OH})$, $\text{CdF}(\text{OH})$ and $\text{Hg}_3\text{O}_2\text{Cl}_2$, $\text{Cd}_3\text{O}_2\text{Cl}_2$ are discussed.



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I. INTRODUCTION

This review summarizes structural studies on some inorganic mercury(II) compounds carried out with X-ray and neutron diffraction techniques. The aim of the single crystal investigations was to determine the bond lengths, the building elements and the coordination polyhedra about the mercury atom, and in the hydrates, to elucidate the hydrogen bonding systems as well. Another intention was to provide a sound basis for a structural comparison with salts of other cations, especially Cd(II). Details of the individual studies have been reported in the following papers:

1. Mercury(II) Chromate.¹
2. A Neutron Diffraction Study of Mercury(II) Chromate Hemihydrate,
 $\text{HgCrO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$.²
3. A Reinvestigation of the Crystal Structures of HgSO_4 and CdSO_4 .³
4. An X-ray and Neutron Diffraction Study of Mercury(II) Sulphate Monohydrate.⁴
5. A Neutron Diffraction Study of Trimerccury(II) Dihydroxide Disulphate Monohydrate, $\text{Hg}_3(\text{OH})_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$.⁵
6. A Neutron Diffraction Study of Mercury(II) Selenate Monohydrate.⁶
7. Refinement of Mercury Fluoride Hydroxide.⁷
8. A Neutron Diffraction Study of $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$.⁸
9. The Crystal Structure of $\text{Hg}_3\text{O}_2\text{Cl}_2$, a Compound with Three-Coordinated Mercury(II).⁹
10. The Crystal Structure of $\text{Hg}_6\text{O}_4\text{Cl}_4$.¹⁰

In 1924 the first structure determination of a mercury(II) compound, HgS (metacinnabarite),^{11,12} was performed. Since then a great number of mercury(II) structures has been solved, and reviewed in three theses by K. Aurivillius (1965),¹³ D. Grdenić (1965)¹⁴ and M. Sandström (1978).¹⁵ A comprehensive report on the structures of mercury compounds, the history of mercury and mercury in industry and pharmacy has been published in a monograph by C.A. McAuliffe (1977).¹⁶

The positions of the lighter atoms, in structures also containing heavy atoms such as mercury, are usually obtained with a rather low accuracy in X-ray structure determinations. This is not only due to the differences in scattering power but

also to the high absorption of X-rays, ($\text{CuK}\alpha$, $\text{MoK}\alpha$) by mercury. Since the early sixties, when computers were beginning to be generally used in the treatment of diffraction data, programmes have been available to calculate corrections for absorption effects by *e.g.* the Gaussian numerical integration method. In spite of this, the absorption correction is even today most often a limiting factor for obtaining high accuracy in heavy atom structures, depending on the problem of correctly describing the shape of the single crystals.

The neutron diffraction technique has been used in the studies of the mercury(II) hydrates presented in *refs.* 2,4,5,6,8. Neutron diffraction is superior to X-ray diffraction for the determination of light atoms, in particular hydrogen atoms, in heavy atom structures, mainly because of the small differences in scattering power of the elements. For most elements, the absorption is also smaller for neutrons than X-rays. There are some drawbacks, however: the single crystals needed, when medium flux reactors (Studsvik, Sweden; Risø, Denmark) are used, must have a volume of some mm^3 , which is at least a thousand times larger than for X-ray diffraction. Growth of such large crystals is often difficult and time-consuming. Furthermore, experiments with neutron diffraction are unfortunately very expensive.

The experimental part of the crystal structure determinations is summarized in chapter II, which also includes the refinement of the structures. A short description of the structures, and some closely related ones, is presented in chapter III. The hydrogen bonds and water molecules in the crystalline hydrates are discussed in chapter IV, and in chapter V a comparison is made between structures of salts of mercury(II) and other cations.

II. EXPERIMENTAL

Preparations

Of the investigated compounds, the chromates, sulphates, the selenate and the fluoride hydroxide can be synthesized from yellow HgO and aqueous solutions of CrO_3 , diluted H_2SO_4 and H_2SeO_4 ¹⁷ and HF .¹⁸ Crystals of HgSO_4 , suitable for the X-ray work, were prepared by treating metallic mercury with hot concentrated sulphuric acid and slowly evaporating the solution at 200°C .¹⁹ As single crystals of $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$ grew very slowly from a solution of yellow HgO in $2.0 \text{ mol l}^{-1} \text{H}_2\text{SeO}_4$, the method of preparing them in gels was tried.²⁰⁻²² Gels of 1.05 g cm^{-3} density were made from solutions of sodium metasilicate in the presence of dilute acetic or nitric acid. U-tubes were used with solutions of mercury nitrate or acetate diffusing into the gels from one end and diluted selenic acid or sodium selenate from the other end. Crystals of the desired compound could, however, not be prepared in this way, but large crystals of three other phases were obtained in the gels, $\text{Hg}_3\text{O}_2\text{SeO}_4$, $\text{Hg}_3(\text{OH})_2(\text{SeO}_4)_2 \cdot \text{H}_2\text{O}$ and another phase, not yet investigated.

The crystals of $\text{Hg}_3\text{O}_2\text{Cl}_2$ and $\text{Hg}_6\text{O}_4\text{Cl}_4$ used in the diffraction work were prepared from a dilute aqueous solution of HgCl_2 hydrolysed by pieces of marble according to Arctowski.²³ $\text{Hg}_3\text{O}_2\text{Cl}_2$ can easily be synthesized in microcrystalline form by boiling a dilute HgCl_2 solution with a deficit of HgO . Small crystals of $\text{Hg}_6\text{O}_4\text{Cl}_4$ were also obtained by heating a mixture of HgO and HgCl_2 in the molar ratio 2:1, moistened with water, in a gold capsule at 3.0 kbar and 250°C , and larger, well shaped crystals were obtained by adding a little HgO to molten HgCl_2 .²⁴

Large single crystals of $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ are readily crystallized from an aqueous solution of HgCl_2 and KCl in the molar ratio 1:2.

Thermal investigations

A preliminary differential thermal analysis (DTA) on the mercury(II) hydrates and the oxide chlorides was made *in vacuo* using a heating rate of 5° min^{-1} . The transformation intervals and residues, examined by powder photographs, are given in Table 1.

The DTA curve for $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ shows two or three peaks, depending on the heating rate, at 90 – 125°C . Thermogravimetric analysis (TGA) indicates that 2/3 of the water content is lost in this temperature interval, and that a complete dehydration occurs at about 160°C . In an earlier DTA investigation, Chihara & Seki²⁵ suggested

a phase transition at 114 °C without dehydration and a complete dehydration at 123 °C. Kiriyaama & Ibamoto²⁶ found a phase transition at 82 °C but no transformation was observed in the temperature range 82-114 °C in a recent IR investigation by Falk & Knop.²⁷ As these statements are full of contradictions a structural investigation of this compound at higher temperatures will be performed in order to ascertain the different phases and to compare their structures. For the dehydrations of the other hydrates see Table 1.

The DTA investigations of $\text{Hg}_3\text{O}_2\text{Cl}_2$ and $\text{Hg}_6\text{O}_4\text{Cl}_4$ showed that both compounds are transformed to $\text{Hg}_5\text{O}_4\text{Cl}_2$, which by further heating decomposes to HgO and HgCl_2 . When $\text{Hg}_3\text{O}_2\text{Cl}_2$ was heated for one week *in vacuo* at about 200 °C, it was converted to $\text{Hg}_6\text{O}_4\text{Cl}_4$, and further heating at 230 °C for three days gave, according to powder photographs, $\text{Hg}_5\text{O}_4\text{Cl}_2$ and HgCl_2 . It thus seems that $\text{Hg}_6\text{O}_4\text{Cl}_4$ and $\text{Hg}_5\text{O}_4\text{Cl}_2$ are the stable phases at about 200° and 230 °C, respectively. The formulae for the changes *in vacuo* are $2\text{Hg}_3\text{O}_2\text{Cl}_2(\text{s}) + \text{Hg}_6\text{O}_4\text{Cl}_4(\text{s}) \rightarrow \text{Hg}_5\text{O}_4\text{Cl}_2(\text{s}) + \text{HgCl}_2(\text{s})$; $\text{Hg}_5\text{O}_4\text{Cl}_2(\text{s}) \rightarrow 4\text{HgO}(\text{s}) + \text{HgCl}_2(\text{s})$.

Table 1. Thermal investigations by DTA and TGA*

Compound	Transformation interval (°C)	Residue
$\text{HgCrO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	185-205	HgCrO_4
$\text{HgSO}_4 \cdot \text{H}_2\text{O}$	50-100	HgSO_4
$\text{Hg}_3(\text{OH})_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$	125-145	$\text{HgSO}_4, \text{Hg}_3\text{O}_2\text{SO}_4$
$\text{HgSeO}_4 \cdot \text{H}_2\text{O}$	75-120	HgSeO_4
$\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$	90-125	$\text{HgCl}_2 \cdot 2\text{KCl} \cdot \frac{1}{3}\text{H}_2\text{O}$
	158-165	$\text{HgCl}_2 \cdot 2\text{KCl}$
$\text{Hg}_3\text{O}_2\text{Cl}_2$	213-260	$\text{Hg}_5\text{O}_4\text{Cl}_2$
$\text{Hg}_6\text{O}_4\text{Cl}_4$	239-268	$\text{Hg}_5\text{O}_4\text{Cl}_2$

*All DTA and TGA analyses were performed at the Arrhenius Laboratory, University of Stockholm.

Unit cell dimensions

Crystal data for the Hg(II)-structures and for the isomorphous Cd-compounds are given in Table 2. The unit-cell dimensions for HgSO_4 , $\text{HgF}(\text{OH})$ and $\text{Hg}_3\text{O}_2\text{Cl}_2$ were calculated from least-squares analyses of θ -values measured on a diffractometer (CAD-4) at room temperature. The unit cell dimensions for the other Hg(II)-compounds were determined from powder photographs taken at room temperature in a Guinier-Hägg camera of radius 50.00 mm, with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$) and KCl ($a = 6.2928 \text{ \AA}$) as an internal standard.

Table 2. Crystal data

Compound	Space group	Z	Unit cell dimensions ($\text{\AA}$, $^\circ$, $\text{\AA}^3$)	
HgCrO_4	$\text{P2}_1/\text{n}$	4	a = 7.356(1) b = 8.528(1) c = 5.502(1)	$\beta = 93.94(2)$ V = 344.3
$\text{HgCrO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	C2/c	8	a = 11.832(1) b = 5.2616(6) c = 14.637(2)	$\beta = 121.01(1)$ V = 781.0
HgSO_4	$\text{Pn2}_1\text{m}$	2	a = 4.7779(2) b = 4.8119(2) c = 6.5720(3)	V = 151.10
CdSO_4	$\text{Pn2}_1\text{m}$	2	a = 4.6982(2) b = 4.7191(2) c = 6.5578(4)	V = 145.40
$\text{HgSO}_4 \cdot \text{H}_2\text{O}$	Pnma	4	a = 7.8796(9) b = 5.4209(5) c = 8.9704(8)	V = 386.17
$\text{Hg}_3(\text{OH})_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$	C2/c	8	a = 7.152(1) b = 8.919(2) c = 14.488(2)	$\beta = 98.94(2)$ V = 912.9
$\text{Hg}_3(\text{OH})_2(\text{SeO}_4)_2 \cdot \text{H}_2\text{O}$	C2/c	8	a = 7.323(2) b = 9.057(2) c = 14.813(4)	$\beta = 100.22(2)$ V = 966.9
$\text{HgSeO}_4 \cdot \text{H}_2\text{O}$	$\text{P2}_1/\text{c}$	4	a = 7.745(1) b = 7.717(1) c = 8.248(2)	$\beta = 119.96(2)$ V = 427.1
$\text{CdSeO}_4 \cdot \text{H}_2\text{O}$	$\text{P2}_1/\text{c}$	4	a = 7.679(2) b = 7.723(2) c = 8.207(2)	$\beta = 120.96(4)$ V = 417.4

Table 2. Continued

Compound	Space group	Z	Unit cell dimensions (Å, °, Å ³)	
HgF(OH)	P2 ₁ 2 ₁ 2 ₁	4	a= 4.9568(6) b= 5.9042(7) c= 6.8630(11)	V=200.85
CdF(OH)	P2 ₁ 2 ₁ 2 ₁	4	a= 4.8320(7) b= 5.5159(7) c= 6.8559(10)	V=182.73
HgCl ₂ ·2KCl·H ₂ O	Pbam	4	a= 8.258(2) b=11.663(2) c= 8.926(2)	V=859.6
Hg ₃ O ₂ Cl ₂	P2 ₁ /c	2	a= 6.3100(7) b= 6.8657(5) c= 6.8579(5)	β= 114.366(6) V= 270.64
Cd ₃ O ₂ Cl ₂	P2 ₁ /c	2	a= 6.3816(7) b= 6.6916(9) c= 6.6651(10)	β= 115.92(1) V= 255.99
Hg ₆ O ₄ Cl ₄	P2 ₁ /c	4	a=10.838(2) b= 9.317(2) c=11.564(2)	β= 108.90(1) V=1104.7

Data collection and reduction

The X-ray data sets were collected at room temperature with a computer-controlled four-circle single-crystal diffractometer (Enraf-Nonius CAD-4). Mo-radiation was used, either Zr-filtered or monochromatized by a graphite monochromator crystal using the (002) planes.

The neutron intensities were measured for HgCl₂·2KCl·H₂O on a Hilger-Ferranti four-circle diffractometer, located at the DR3 reactor of the Danish Atomic Energy Commission Research Establishment, Risø, Denmark. For the other hydrates, neutron diffraction data were collected at the Swedish Atomic Energy reactor R2, Studsvik, with a Hilger & Watts computer-controlled four-circle diffractometer. The flux at the specimen was about 10⁶ neutrons cm⁻² s⁻¹ for both reactors and the wavelengths of the monochromatized neutron beam were 1.025 Å (Risø) and 1.210 Å (Studsvik).

The X-ray and neutron intensities were measured with the ω - or ω -2 θ scan techniques with maximum scan times of 5 min (X-ray) and 20 min (neutrons). In each experiment a few standard reflexions were used to provide a check on the stability of crystal and electronics. Corrections were applied to the intensities for Lorentz, polarization (X-ray) and absorption effects, and the transmission factors were evaluated by Gaussian numerical integration according to Busing & Levy.^{28,29} The absorption coefficients in the neutron diffraction studies were measured at the reactor or calculated assuming a value of 40 barns for the incoherent scattering cross-section of hydrogen.

Determination and refinement of the structures

The mercury atoms in HgCrO_4 , HgSO_4 , $\text{HgF}(\text{OH})$ and $\text{Hg}_3\text{O}_2\text{Cl}_2$ (X-ray data) were determined from three-dimensional Patterson maps, and the other atoms from subsequent difference Fourier syntheses. The structure of $\text{Hg}_6\text{O}_4\text{Cl}_4$ was solved from X-ray data and that of $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$ from neutron data by direct methods. For the hydrates $\text{HgCrO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{HgSO}_4 \cdot \text{H}_2\text{O}$, $\text{Hg}_3(\text{OH})_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ (neutron data), the positions of the non-hydrogen atoms were taken from previous determinations by Aurivillius,³⁰ Templeton *et al.*,³¹ Björnlund,³² and Aurivillius & Stålhandske,³³ and the hydrogen atoms were found from difference syntheses.

All structure refinements were made by full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$, where w is the weight calculated from the expression $w^{-1} = \sigma_c^2(|F_o|^2)/4|F_o|^2 + C_1|F_o|^2 + C_2$. The parameters C_1 and C_2 were adjusted until the averages of $w(\Delta F)^2$ were close to unity in different intervals of $|F_o|$ and $\sin\theta$. In the final refinements, a parameter to correct for isotropic secondary extinction (Zachariasen³⁴) was included. Some data on the crystal structures and the refinements are given in Table 3.

The atomic scattering factors were taken from Doyle & Turner³⁵ for the non-hydrogen atoms and from Stewart *et al.*³⁶ for hydrogen. Anomalous dispersion parameters were those of Cromer & Liberman.³⁷ In the refinements of the neutron diffraction data, some of the coherent scattering amplitudes were included as parameters; others were fixed at the values given by Bacon.³⁸ Most calculations were carried out on the UNIVAC 1108 computer in Lund, using programmes briefly described by Svensson.³⁹

Table 3. Data collections and refinements

Technique: X = X-ray data, N = neutron data. Absorption coefficient μ_λ in cm^{-1} and crystal volume V in mm^3 . T denotes transmission range, m the number of reflexions used, n the number of parameters refined and R is the reliability index in %. σ_{dist} gives the largest e.s.d.'s ($\text{\AA} \times 10^3$) in Hg-O or Hg-Cl distances.

Compound		μ_λ	V	T	m	n	R	σ_{dist}	Ref
HgCrO_4	X	487	0.0045	0.009-0.056	1163	36	4.9	10	1
$\text{HgCrO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	N	2.84	5.5	0.54-0.73	870	72	3.0	2	2
HgSO_4	X	524	0.0005	0.03-0.17	1092	34	3.3	9	3
CdSO_4	X	80	0.0012	0.47-0.67	791	34	1.3	3	3
$\text{HgSO}_4 \cdot \text{H}_2\text{O}$	X	414	0.010	0.004-0.050	1182	41	4.0	7	4
	N	3.59	27	0.38-0.53	499	56	3.2	2	4
$\text{Hg}_3(\text{OH})_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$	N	3.80	19	0.36-0.56	1178	94	2.8	2	5
$\text{HgSeO}_4 \cdot \text{H}_2\text{O}$	N	3.38	5.4	0.57-0.67	904	85	2.6	1	6
$\text{HgF}(\text{OH})$	X	778	0.0022	0.005-0.047	441	19	6.6	21	7
$\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$	N	1.67	253	0.34-0.56	2181	54	4.7	1(Cl)	8
$\text{Hg}_3\text{O}_2\text{Cl}_2$	X	869	0.0014	0.007-0.039	669	35	5.9	14(O) 5(Cl)	9
$\text{Hg}_6\text{O}_4\text{Cl}_4$	X	857	0.0007	0.015-0.066	1859	88	5.9	22(O) 8(Cl)	10

III. DESCRIPTION OF THE STRUCTURES

This chapter gives a short review of the structural chemistry of solid Hg(II) compounds containing Hg-O, Hg-F and Hg-Cl bonds, with emphasis on the structures in this work. The hydrogen bonds in the hydrates are discussed in chapter IV.

Structures of mercury(II) compounds have earlier been reviewed in theses by K. Aurivillius (1965)¹³ and D. Grdenić (1965).¹⁴ More recently mercury(II)-oxygen and mercury(II)-halogen coordinations have been tabulated in a thesis by M. Sandström (1978).¹⁵ Crystallographic and spectroscopic data for complexes of the type (L)HgX₂ and (L)₂HgX₂ (where L = neutral unidentate ligand; X = Cl, Br or I) have been summarized in a thesis by T. Jones (1979).⁴⁰

The electronic configuration of mercury in the ground state is (Xe-core)-4f¹⁴5d¹⁰6s², and from the ionization potentials it is obvious that under chemical conditions no more than two electrons can be removed. From the simple ionic theory, in which the ions are regarded as non-polarizable spheres, a high coordination number is predicted for large cations such as Hg²⁺. However, mercury(II) exhibits a strong tendency to coordinate two ligands by short bonds in a linear or nearly linear way, unlike the other group IIB elements zinc and cadmium with dominating coordination numbers four and six. As mercury is one of the most electronegative metals, covalent bonding dominates in many Hg(II) compounds. Orgel⁴¹ has suggested that the two-coordination of Hg(II) is only partly due to the large s-p energy separation, which favours the formation of a small number of bonds. He proposed a mechanism involving d-s mixing, which requires much less energy for Hg(II) than for Cd(II) and Zn(II). An effect related to the Jahn-Teller distortion favours two strong linear bonds, and perpendicular to them four weak bonds, resulting in a distorted octahedral coordination. This is the most frequent polyhedron around Hg, but others are not unusual, e.g. trigonal or pentagonal bipyramids with the apical atoms strongly bonded.

The metallic radius of mercury is 1.50 Å derived from crystalline mercury,⁴² α-Hg, in which each atom has six neighbours at 2.993 Å and six more at 3.465 Å. Grdenić¹⁴ used the value 1.50 Å for the van der Waals radius of mercury as well, r_w(Hg), as this value is expected to be nearly equal to the metallic radius. From the critical volume of Hg, Bondi⁴³ estimated the van der Waals radius to be 1.55 Å.

A commonly used classification of the coordination about mercury in terms of *characteristic* and *effective* coordination numbers has been suggested by Grdenić.¹⁴ The mercury atom has its *characteristic* coordination number when all mercury-ligand

bond lengths are of the same magnitude. All ligands closer to the mercury atoms than the sum of the corresponding van der Waals radii are included in the *effective* coordination sphere. This classification is also used in this thesis, although other definitions of the coordination number exist.⁴⁴

Mercury-oxygen coordination

The oxide Hg-O exists in at least two modifications, one orthorhombic and one trigonal. Both structures are built up of endless zig-zag -O-Hg-O-Hg- chains^{45,46} with two short Hg-O bonds [2.03-2.07 Å], the orthorhombic structure by planar and the trigonal by spiral chains (Fig. 1). The O-Hg-O angles are close to 180° and the Hg-O-Hg angles are close to 109°. In both compounds there are four additional oxygen atoms at distances [2.79-2.90 Å] shorter than or equal to the sum of the van der Waals radii [$r_w(\text{Hg}) = 1.50$,¹⁴ $r_w(\text{O}) = 1.40$ Å⁴⁷]. The orthorhombic modification of mercury(II) peroxide, $\beta\text{-HgO}_2$,⁴⁸ also consists of endless chains formed from the mercury atoms and the peroxide groups. Also for this compound four more oxygen atoms complete a distorted octahedron around Hg (*cf.* chap. V).



Fig. 1. The infinite chains in (a) HgO(orth) and (b) HgO(trig).

Infinite chains are building elements for many other mercury(II) structures with Hg-O bonds.⁴⁹⁻⁵¹ Of the structures studied here the two chromates, HgCrO_4 ¹ and $\text{HgCrO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$,² are built up of endless chains with mercury digonally coordinated by oxygen [2.05-2.12 Å; 163, 176°] (Fig. 2a,b). In both compounds the chains are connected to three-dimensional networks by five weaker Hg-O contacts [2.48-2.79 Å], giving an effective coordination number of 7. The polyhedra around mercury are distorted pentagonal bipyramids. In $\text{HgCrO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, chains of composition $[\text{HgCrO}_4]_n$ are in addition linked by weak hydrogen bonds (*cf.* chap. IV).

A preliminary investigation of $\text{Hg}_3\text{O}_2\text{CrO}_4$ shows, as suggested by Aurivillius & Malmros,¹⁷ that the compound is isostructural with the corresponding sulphate $\text{Hg}_3\text{O}_2\text{SO}_4$.⁵² $\text{Hg}_3\text{O}_2\text{CrO}_4$ is built up of infinite -Hg-O-Hg- chains condensed by additional Hg atoms to folded layers with formula $[\text{Hg}_3\text{O}_2]_n^{2n+}$ (Fig. 2c) and with chromate ions, possibly disordered, in the cavities in the layers.

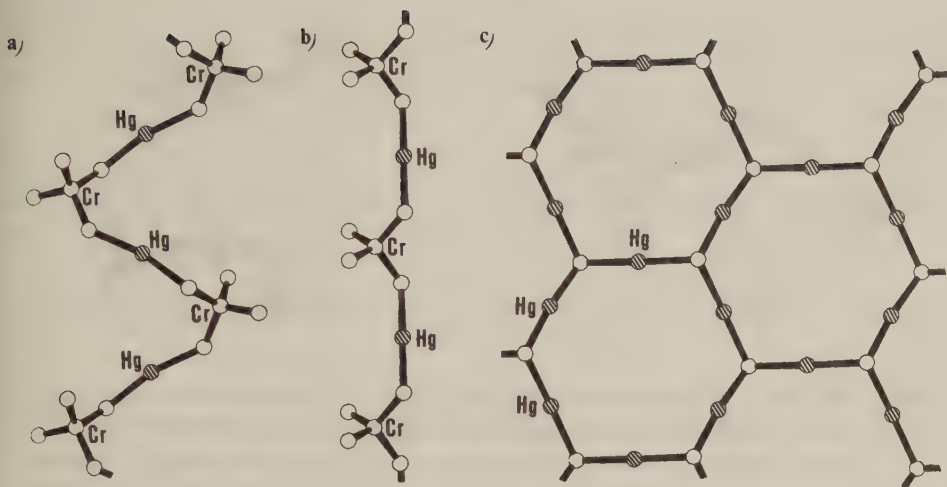


Fig. 2. Endless chains in (a) HgCrO_4 and (b) $\text{HgCrO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. Layers of formula $(\text{Hg}_3\text{O}_2)_n^{2n+}$ in (c) $\text{Hg}_3\text{O}_2\text{CrO}_4$.

Of the four existing mercury(II) sulphates $\text{Hg}_3\text{O}_2\text{SO}_4$, $\text{Hg}_3(\text{OH})_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{HgSO}_4 \cdot \text{H}_2\text{O}$ and HgSO_4 , the first as mentioned is isomorphous with $\text{Hg}_3\text{O}_2\text{CrO}_4$ and $\text{Hg}_3\text{O}_2\text{SeO}_4$. The compound $\text{Hg}_3(\text{OH})_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ is the first structure studied, in which the building element is a finite zig-zag chain.³² In the chains $\text{SO}_4\text{-Hg-OH-Hg-OH-Hg-SO}_4$ (Fig. 3a) the two independent mercury atoms are two-coordinated, one linearly [2.15 Å] and the other [2.06, 2.09 Å] with an O-Hg-O angle of 169° .⁵ The coordination polyhedra are a distorted octahedron with four weaker bonds [Hg-O 2.46-2.47 Å] and a very distorted trigonal bipyramid with three weak bonds [Hg-O 2.65-2.73 Å]. The chains are further connected by hydrogen bonds between the hydroxide groups and the water molecule (*cf.* chap. IV).

The monohydrate, $\text{HgSO}_4 \cdot \text{H}_2\text{O}$, has been studied by Bonefačić⁵³ and by Templeton *et al.*³¹ and refined from X-ray and neutron data by the present author.⁴ The mercury atom has the usual digonal coordination with the two short bonds to one sulphate oxygen atom [2.18 Å] and one water molecule [2.23 Å] with a bond angle of 169° , forming a discrete molecule (Fig. 3b). Four Hg-O contacts [2.50-2.51 Å] complete a distorted octahedron around mercury. Hydrogen bonds link the $\text{SO}_4\text{-Hg-OH}_2$ groups to a three-dimensional structure (*cf.* Fig. 10).

Discrete mercury-sulphate complexes have also been found in the structure of $\text{Ti}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$,⁵⁴ with mercury digonally coordinated in the two anions

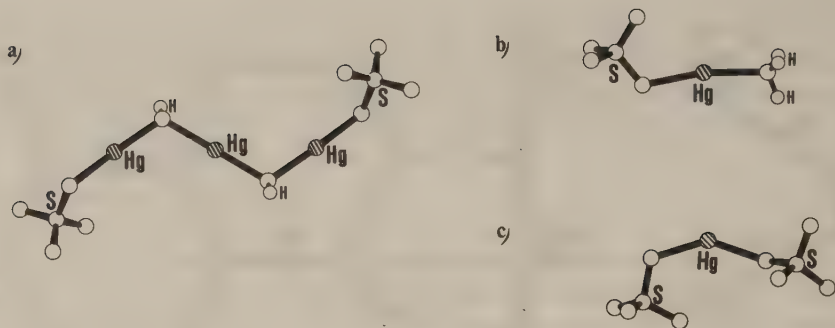


Fig. 3. (a) The finite chain in $\text{Hg}_3(\text{OH})_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. (b) The molecule in $\text{HgSO}_4 \cdot \text{H}_2\text{O}$. One of the water hydrogen atoms is disordered, occupying two positions, both of which are shown in the drawing. (c) The discrete $\text{Hg}(\text{SO}_4)_2^{2-}$ complex in $\text{Tl}_3[\text{Hg}(\text{SO}_4)_2][\text{HgSO}_4\text{Cl}]$.

$[\text{Hg}(\text{SO}_4)_2]^{2-}$ (Fig. 3c) [Hg-O 2.09, 2.16 Å] and $[\text{Hg}(\text{SO}_4)\text{Cl}]^-$ [Hg-O 2.17; Hg-Cl 2.24 Å]. The bond angle at the mercury atom deviates considerably from linearity [144, 159°] in both anions.

In the mercury(II) compounds described up to this point, the characteristic coordination number of the metal atom is two, which is the prevalent case for Hg-O coordination. Three-coordination is rare, but is found in HgTiO_3 ⁵⁵ [Hg-O 2.20 Å], a compound which can be prepared only at high pressure and high temperature (65 kbar, 800–1100 °C), and in $\text{Hg}_3\text{O}_2\text{Cl}_2$ [Hg-O 2.17, 2.32, 2.33 Å] (p. 19).

Four-coordination exists in HgTeO_6 [Hg-O 2.33 Å]⁵⁶ and also in $\text{Hg}(\text{OHg})_4\text{Br}_2$,⁵⁷ where one of the three independent Hg atoms is tetrahedrally [Hg-O 2.24 Å] and the other two digonally bonded [Hg-O 2.04 Å; 163, 176°]. Mercury is also four-coordinated in HgSO_4 .^{3,19,58} The structure is built up of very distorted HgO_4 tetrahedra and SO_4 groups sharing corners (Fig. 4). Two Hg-O distances are shorter [2.22 Å] than the others [2.28, 2.42 Å], indicating the tendency of mercury to form the usual two-coordination.

Six-coordination for mercury was first found in $[\text{Hg}(\text{C}_6\text{H}_5\text{NO})_6](\text{ClO}_4)_2$,⁵⁹ which consists of $\text{Hg}(\text{C}_6\text{H}_5\text{NO})_6^{2+}$ and ClO_4^- ions with a regular octahedral coordination about Hg [Hg-O 2.35 Å]. X-ray diffraction studies on acidic aqueous solutions of Hg(II) have revealed $\text{Hg}(\text{H}_2\text{O})_6^{2+}$ ions^{60,61} with a regular octahedral structure [Hg-O 2.41 Å] and recently the same complex was found in the solid compound $[\text{Hg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ [Hg-O 2.34 Å].⁶² The mercury(II) selenates are, as expected isostructural with the

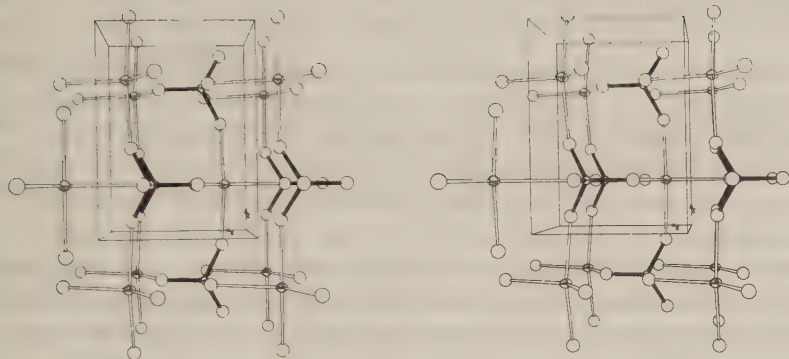


Fig. 4. The structure of HgSO_4 . Bonds Hg-O are open and S-O filled.

corresponding sulphates, except for $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$.⁶ In this compound, Hg is also six-coordinated [Hg-O 2.26–2.50 Å]. The structure is built up of distorted $\text{HgO}_4(\text{OH}_2)_2$ octahedra and SeO_4 tetrahedra. Each octahedron comprises four oxygen atoms from four different selenate groups, and two water molecules. The octahedra are connected by the water molecules to form endless chains (Fig. 5), running in the *c*-direction, further linked by the selenate groups and hydrogen bonds.

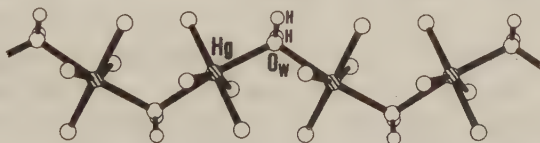


Fig. 5. The endless chains of corner-shared octahedra in the structure of $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$.

A characteristic mercury-oxygen coordination number higher than six has so far been reported only for the compound $\text{K}_3[\text{Hg}(\text{NO}_2)_4]\text{NO}_3$,^{63,64} containing $[\text{Hg}(\text{NO}_2)_4]^{2-}$ and NO_3^- as discrete anions. The eight oxygen atoms of the four coordinated nitrito groups form a highly distorted square antiprism about mercury, with Hg-O bond lengths of 2.39–2.57 Å. High coordination numbers are also found in a preliminary structure investigation of two mercury(II) bromates. In one of them, $\text{Hg}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$, the mercury atom is coordinated by eight oxygen atoms, two from water molecules [Hg-O 2.33, 2.34 Å] and six from four different bromate groups [Hg-O 2.43–2.72 Å].

Mercury-fluorine coordination

Of the mercury(II) halides, the fluoride has the fluorite (CaF_2) structure, probably with dominating ionic bonding, while in the other halides covalent bonding is prevalent. Only a few mercury-fluorine compounds have so far been investigated. Except for HgF_2 ⁶⁵ and some ternary compounds, *e.g.* RbHgF_3 ,⁶⁶ HgMnF_6 ⁶⁷ and HgSnF_6 ⁶⁸ studied from X-ray powder data, only the structures of $\text{HgF}_2 \cdot 2\text{H}_2\text{O}$ ⁶⁹ and $\text{HgF}(\text{OH})$ ⁷⁶ have been determined. In both HgF_2 and $\text{HgF}_2 \cdot 2\text{H}_2\text{O}$ the mercury atoms are eight-coordinated. In HgF_2 the polyhedron around Hg is a cube [2.40 Å], and in $\text{HgF}_2 \cdot 2\text{H}_2\text{O}$ a distorted Archimedean antiprism with four oxygen and four fluorine atoms [Hg-O, F 2.27–2.61 Å]. In $\text{HgF}(\text{OH})$ the mercury atom is coordinated to two hydroxide groups [2.10, 2.12 Å, 177°], forming endless zig-zag chains of formula $[\text{Hg}(\text{OH})]_n^{n+}$ (Fig. 6) and with a Hg-O-Hg angle of 109°. The same type of chain has earlier been found in

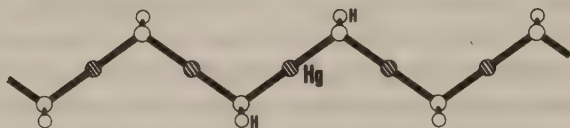


Fig. 6. The infinite $[\text{Hg}(\text{OH})]_n^{n+}$ chain in $\text{HgF}(\text{OH})$.

e.g. $\text{Hg}(\text{OH})\text{BrO}_3$ ⁷⁰ and $\text{Hg}(\text{OH})\text{NO}_3$,⁵¹ but in both these compounds the O-Hg-O angles are smaller [175, 172°], and the angles Hg-O-Hg are larger [123, 120°]. The chains in $\text{HgF}(\text{OH})$ are linked by hydrogen bonds O-H...F of 2.52 Å. Three fluorine atoms [Hg-F 2.49–2.50 Å] and one additional oxygen atom [2.69 Å] complete a distorted octahedron around mercury. The structure is of the rutile type with the anions in an approximate hexagonal close-packing (*cf.* chap. V).

Mercury-chlorine coordination

The characteristic coordination number for Hg in mercury-chlorine compounds is often 2, but 3 to 5 also exist. Two-coordination is found in HgCl_2 ,^{71,72} built up of almost linear Cl-Hg-Cl molecules [Hg-Cl 2.28 Å, 179°].⁷³ The six next nearest neighbours to Hg are at distances [Hg-Cl 3.37–3.48 Å] longer than the sum of the van der Waals radii [3.30 Å].^{14,47} The structure of $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ ⁸ also consists of digonally coordinated Hg atoms [Hg-Cl 2.38 Å, 170°]. Four additional chlorine atoms [2×2.80, 2×3.25 Å] give a distorted octahedron around Hg. These polyhedra share edges forming chains, running along [001], joined by hydrogen bonds from the water molecules (Fig. 13). Distorted HgCl_6 octahedra, with two short bonds and four

longer ones, are found in many mercury-chlorine compounds. The polyhedra can be linked to double chains as found in $\text{NaHgCl}_3 \cdot 2\text{H}_2\text{O}$ ⁷⁴ and $\text{NH}_4\text{HgCl}_3 \cdot \text{H}_2\text{O}$ ⁷⁵ or to infinite sheets as in $\alpha\text{-NH}_4\text{HgCl}_3$.⁷⁶

Three-coordination is also fairly common, and is found in *e.g.* $[\text{S}_4\text{N}_3]\text{HgCl}_3$ ⁷⁷ and $\alpha\text{-}[\text{N}(\text{C}_2\text{H}_5)_4]\text{HgCl}_3$ ⁷⁸ with planar HgCl_3 units and with two longer Hg-Cl contacts completing a trigonal bipyramidal configuration around Hg.

Four-coordination is unusual and is found for the tetrahedral HgCl_4^{2-} ions in Cs_3HgCl_5 ⁷⁹ and $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_3[\text{HgCl}_4] \cdot 2\text{H}_2\text{O}$,⁸⁰ with a mean Hg-Cl distance of 2.48 Å. Recently in $[\text{N}(\text{C}_4\text{H}_9)_4][\text{Hg}_2\text{Cl}_6]$ ⁸¹ discrete dimeric $\text{Hg}_2\text{Cl}_6^{2-}$ ions are also found, in which two HgCl_4 tetrahedra share an edge.

The highest characteristic coordination number for Hg with Cl as ligand is five, found in $[\text{Cr}(\text{NH}_3)_6][\text{HgCl}_5]$,⁸² which is built up of octahedral $\text{Cr}(\text{NH}_3)_6^{3+}$ ions and trigonal bipyramidal HgCl_5^{3-} ions with two axial Hg-Cl bonds shorter [2.52 Å] than the three equatorial bonds [2.64 Å].

The crystal chemistry of mercury oxide chlorides with formula $n\text{HgO} \cdot \text{HgCl}_2$ ($n = \frac{1}{2}, 2, 4$) has been the object of several single-crystal investigations. The compound Hg_3OCl_4 ($n = \frac{1}{2}$)^{83,84} is built up of Cl^- ions and discrete trinuclear pyramidal ions $\text{OHg}_3\text{Cl}_3^+$ (Fig. 7a), with the oxygen atom at the apex of the flattened pyramid, and the chlorine atoms forming the base. The O-Hg-Cl groups are almost linear [176°] with Hg-O and Hg-Cl distances of 2.05 and 2.30 Å. The compound $2\text{HgO} \cdot \text{HgCl}_2$ is dimorphous; both structures have been solved and the stability relationships studied. The compounds formulated as $\text{Hg}_3\text{O}_2\text{Cl}_2$ and $\text{Hg}_6\text{O}_4\text{Cl}_4$ ($3\text{-Hg}_3\text{O}_2\text{Cl}_2$) are both monoclinic, but structurally different.

In $\text{Hg}_3\text{O}_2\text{Cl}_2$ ⁹ there are two independent mercury atoms, one linearly coordinated to oxygen [2.07 Å] and the other bonded to three oxygen atoms [2.17, 2.32 and 2.33 Å] with the nearest chlorine atom at 2.71 Å. As the latter distance is appreciably longer than 2.48 Å, found for Hg-Cl four-coordination, this Hg atom is considered three-coordinated. $\text{Hg}_3\text{O}_2\text{Cl}_2$ can be described as endless sheets of linked flattened HgO_3 pyramids (Fig. 7b), connected by the two-coordinated Hg-atoms and by weak Hg-Cl bonds.

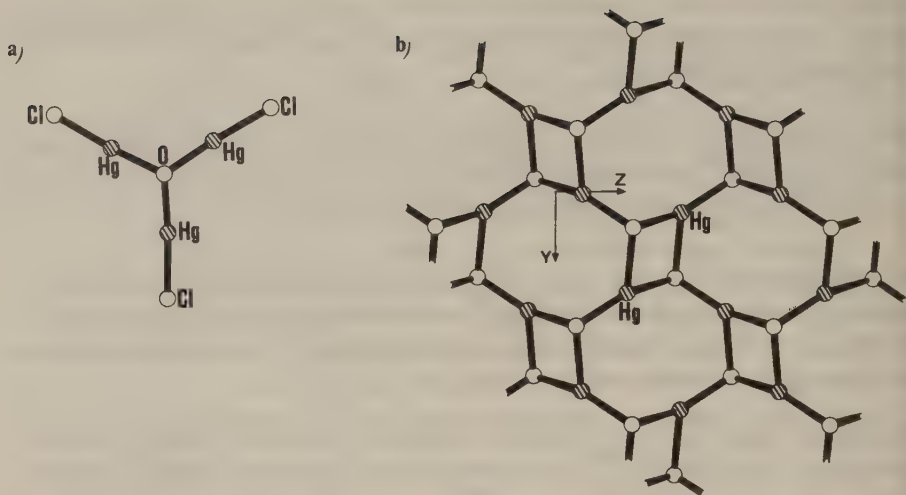


Fig. 7. (a) The $\text{OHg}_3\text{Cl}_3^+$ ions in Hg_3OCl_4 .

(b) Endless sheets of linked flattened HgO_3 pyramids in $\text{Hg}_3\text{O}_2\text{Cl}_2$. The sheets are connected by linearly coordinated mercury atoms bonded to the oxygen atoms.

Two independent X-ray studies of $\text{Hg}_6\text{O}_4\text{Cl}_4$ with the same accuracy have been published.^{10,85} The structure of the compound is complicated, and very different from that of $\text{Hg}_3\text{O}_2\text{Cl}_2$. It can be described in various ways. Fundamental building elements of the structure are infinite $-\text{O}-\text{Hg}-\text{O}-$ chains of the same type as found in $\text{Hg}(\text{OHg})_4\text{Br}_2$,⁵⁷ isomorphous with $\text{Hg}(\text{OHg})_4\text{Cl}_2$ ($n = 4$). In the latter compounds the four two-coordinated Hg-atoms form chains (Fig. 8a) connected by the fifth Hg atom, which is tetrahedrally coordinated. In $\text{Hg}_6\text{O}_4\text{Cl}_4$ four of the six Hg atoms are involved in chains and the fifth Hg atom is incorporated *via* a $-\text{Hg}-\text{Cl}$ side chain (Fig. 8b). Two such chains are connected to double chains of formula $[\text{Hg}_2(\text{OHg})_4\text{Cl}^{3+}]_n$ by the sixth Hg atom. These double chains are further linked by weaker Hg-O contacts. The structure description can also be based on the arrangement of mercury atoms around the oxygens, the compound in this way built up of distorted Hg_4O tetrahedra, linked into a three-dimensional array.

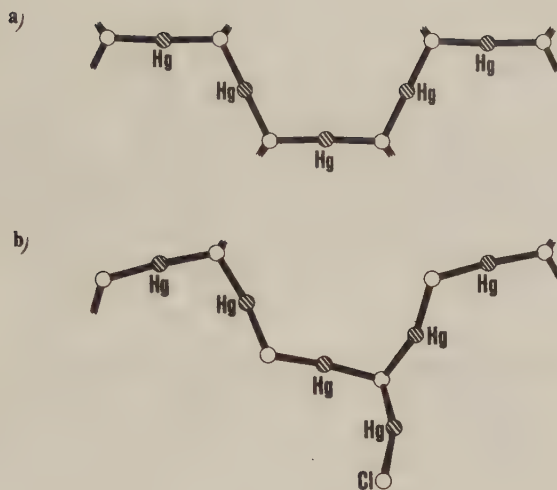


Fig. 8. (a) Infinite chains in $\text{Hg}(\text{OHg})_4\text{Br}_2$.
 (b) Infinite single chains in $\text{Hg}_6\text{O}_4\text{Cl}_4$.

IV. THE CRYSTALLINE HYDRATES

The role of the water molecules

The structures of the five hydrates investigated have all been refined from neutron diffraction data, and the hydrogen atoms are thus located with high accuracy. Although none of them crystallizes with more than one water molecule per formula unit, the water molecules play an important role by linking structural elements *via* hydrogen bonds. For the thermal investigations of these compounds by DTA and TGA, cf. Table 1.

In $\text{HgSO}_4 \cdot \text{H}_2\text{O}^4$ and $\text{HgSeO}_4 \cdot \text{H}_2\text{O}^6$ the water molecules are directly bonded to Hg (Figs. 3b, 9). Upon dehydration, these compounds are reconstructively converted to the isomorphous HgSO_4 and HgSeO_4 , which are built up completely differently from either of the hydrates. In $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$, corner sharing $\text{HgO}_4(\text{OH}_2)_2$ octahedra form chains (Fig. 5) running in the *c*-direction. The chains are connected by SeO_4 groups and hydrogen bonds between the water molecules and selenate O atoms to form a three-dimensional structure (Fig. 9).

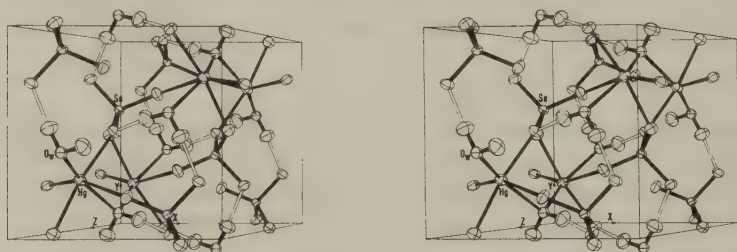


Fig. 9. The structure of $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$. The acceptor bonds in the drawing are open, other bonds are filled.

Crystals of both $\text{Hg}_3(\text{OH})_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}^5$ and $\text{HgSO}_4 \cdot \text{H}_2\text{O}^4$ can be described as built up of discrete molecules (Fig. 3a,b). In $\text{HgSO}_4 \cdot \text{H}_2\text{O}$ one set of hydrogen bonds from the water molecules connects the $\text{HgSO}_4 \cdot \text{H}_2\text{O}$ groups to endless folded chains in the *a*-direction (Fig. 10). The other hydrogen atoms (H2), statistically distributed across mirror planes, link one chain to adjacent parallel chains by hydrogen bonds to the water oxygens, forming a three-dimensional structure.

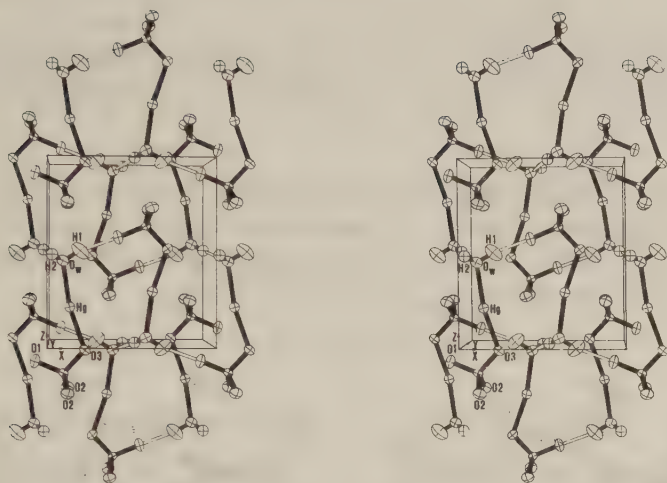


Fig. 10. The structure of $\text{HgSO}_4 \cdot \text{H}_2\text{O}$. For clarity only one of the statistically distributed hydrogen atoms (H2) is included, and with an artificial isotropic temperature factor.

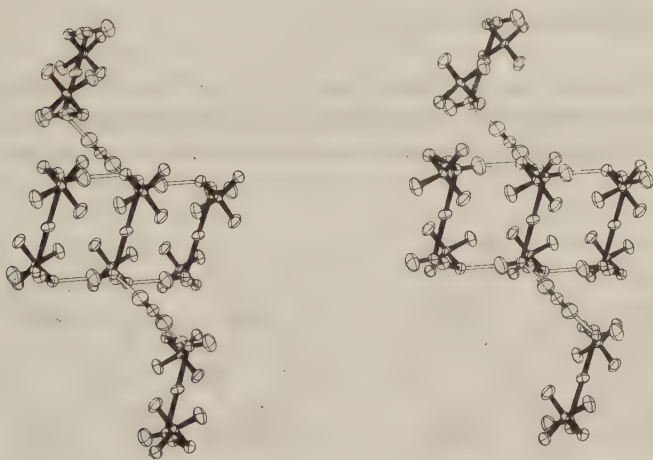


Fig. 11. $\text{Hg}_3(\text{OH})_2(\text{SO}_4)_2$ and water molecules connected by hydrogen bonds.

Also in the compound $\text{Hg}_3(\text{OH})_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ hydrogen bonds connect the discrete molecules to a three-dimensional network. Fig. 11 shows how each finite $\text{SO}_4\text{-Hg-OH-Hg-OH-Hg-SO}_4$ chain is linked to four different chains *via* the water molecules and the hydroxide groups. On dehydration it is decomposed to HgSO_4 and $\text{Hg}_3\text{O}_2\text{SO}_4$ (Table 1).

In the structure of $\text{HgCrO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ⁷ water molecules bind the endless "linear" $\text{-CrO}_4\text{-Hg-CrO}_4\text{-Hg-}$ chains together by weak hydrogen bonds to slabs of thickness $c/2$ (Fig. 12). After dehydration HgCrO_4 is formed, built up of endless $[\text{HgCrO}_4]_n$ chains of the "zig-zag" type (Fig. 2a).

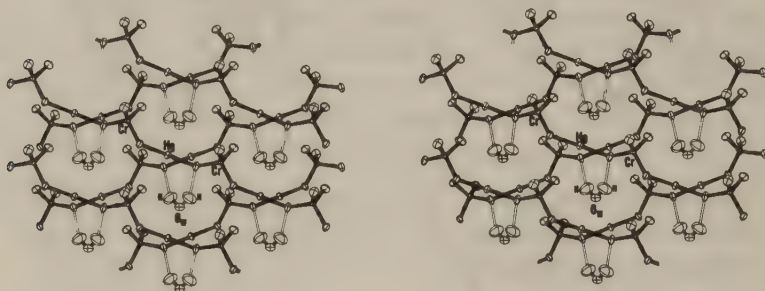


Fig. 12. Part of the structure of $\text{HgCrO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$.

Fig. 13 shows a part of the structure of $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ ⁸ in which weak hydrogen bonds from the water molecules connect chains of edge-sharing HgCl_6 octahedra. It seems as if this compound can be partially dehydrated without a complete collapse of the lattice.

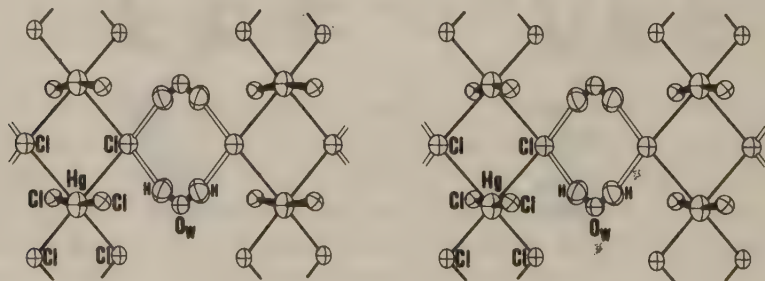


Fig. 13. Part of the structure of $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$.

Hydrogen bonds

A normal hydrogen bond can be said to exist when a covalently bonded hydrogen atom interacts with another atom. The hydrogen bond thus involves a donor atom X, a hydrogen atom H and an acceptor atom A, as shown in Fig. 14. The distance X-H is called the donor distance (d), H...A the acceptor distance (a) and X...A is the hydrogen bond distance (R). The hydrogen bond angle, X-H...A, is denoted θ . If the



Fig. 14. The hydrogen bond parameters.

hydrogen atoms are accurately located, as in neutron diffraction work, a hydrogen bond is assumed to exist if the acceptor distance is shorter than the sum of the van der Waals radii of H and A. The most frequently used value of $r_w(O)$ is 1.4 Å, given by Pauling,⁴⁷ and the currently accepted value of $r_w(H)$ is 1.0 Å, suggested by Baur.⁸⁶ A geometrical criterion for a hydrogen bond O...O is thus an acceptor distance O...H shorter than 2.4 Å. Close to this limit it is not possible to decide from such geometrical considerations alone if a hydrogen bond occurs, and longer acceptor distances have been reported. For the detection of such very weak interactions, IR spectroscopy affords a more sensitive technique.

The geometry of the hydrogen bonds and water molecules in the structures studied are summarized in Table 4. All hydrogen bonds are non-linear, with θ -values varying between 146 and 173°. Of the seven O-H...O bonds, six give θ -values in the interval 167-173°. These θ -values are close to the highest frequency θ -interval of 165-170° in a histogram by Ferraris & Franchini-Angela⁸⁷ based on data from 41 crystalline hydrates studied by neutron diffraction. Kroon & Kanters⁸⁸ have constructed a histogram from another series of 196 values of hydrogen bond angles, which gives a maximum in the θ -interval 160-165°. These distributions seem to be inconsistent with theoretical calculations,^{89,90} which have shown that at least for O-H...O hydrogen bonds, the configuration of minimum energy involves a linear hydrogen bond ($\theta=180^\circ$). However, Pedersen⁹¹ and Kroon & Kanters⁸⁸ have pointed out that before observed angle distributions of hydrogen bonds are compared to results from theoretical calculations, the number of bonds in each θ -interval must be divided by a geometrical factor. This factor, which is the area of the spherical segment between the limits of each θ -interval in the histogram, is proportional to $\sin\theta$. New histo-

Table 4. The geometry of the water molecules and hydrogen bonds.

X denotes O or Cl

Compound	O-H/Å	>H-O-H/°	O...X/Å	H...X/Å	>O-H...X/°	Donor	Acceptor
HgCrO ₄ ·1/2 H ₂ O	0.945(4)	103.7(4)	2.961(2)	2.133(4)	145.6(3)	H ₂ O	CrO ₄
HgSO ₄ ·H ₂ O	0.931(9)	108.0(6)	3.184(2)	2.264(9)	170.0(8)	H ₂ O	H ₂ O
	0.955(5)		2.849(3)	1.902(5)	170.6(5)	H ₂ O	SO ₄
Hg ₃ (OH) ₂ (SO ₄) ₂ ·H ₂ O	0.972(2)	105.8(3)	2.829(2)	1.863(3)	172.3(3)	H ₂ O	OH
	0.979(3)		2.832(2)	1.860(3)	171.3(3)	OH	SO ₄
HgSeO ₄ ·H ₂ O	0.983(2)	104.8(2)	2.734(1)	1.756(2)	172.9(2)	H ₂ O	SeO ₄
	0.984(2)		2.706(2)	1.738(2)	167.3(2)	H ₂ O	SeO ₄
HgCl ₂ ·2KCl·H ₂ O	0.948(2)	107.9(3)	3.249(1)	2.329(2)	163.6(2)	H ₂ O	Cl

grams, corrected for the $\sin\theta$ dependence, show a maximum for θ in the interval 175–180° and are thus in good agreement with the theoretically found preference for a linear hydrogen bond.

The O-H...O hydrogen bonds in the hydrates are weak or of intermediate strength with O...O distances of 2.71–3.18 Å and acceptor distances in the range 1.74–2.26 Å (Table 4). Novak⁹² has in a review of spectroscopic studies of hydrogen bonds concluded that a qualitative change in the character of the bond occurs in the range 2.6 to 2.7 Å. Furthermore, from a bond-valence analysis of the repulsion between the O atoms in O-H...O hydrogen bonds Brown⁹³ has suggested that hydrogen bonds shorter than 2.7 Å are strong, involve strain and are linear, while those longer than 2.7 Å are weak and generally bent. From the bond-valence analysis, Brown predicted a correlation between H...O acceptor distances and O-H...O bond angles. This correlation curve is included in Fig. 15, which contains acceptor distances and bond angles from the hydrates. The largest deviation from the correlation curve is found for the hydrogen bond in HgSO₄·H₂O, which involves the disordered hydrogen atom, and for the hydrogen bonds in HgCrO₄· $\frac{1}{2}$ H₂O. In the latter compound the deviation is probably due to the crystal packing arrangement, which results in an extremely small value of 55° for the acceptor angle O...O_w...O.

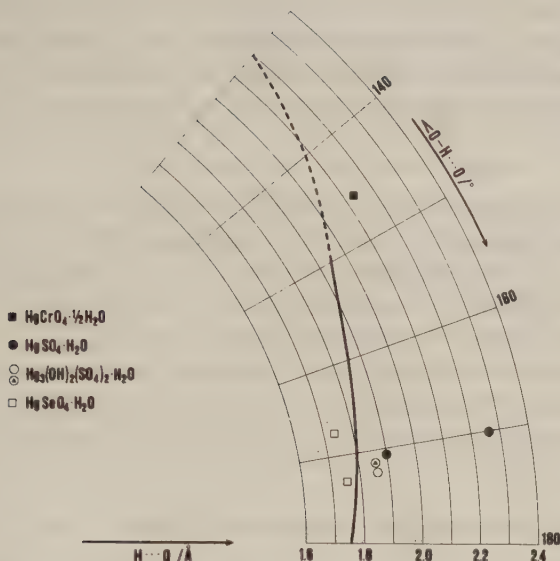


Fig. 15. The correlation between the $\text{O} \cdots \text{H}$ acceptor distances and $\text{O-H} \cdots \text{O}$ bond angles in the hydrates. The correlation curve is that predicted by Brown.⁹³

Water molecules and their environments

Ferraris & Franchini-Angela⁸⁷ found variations in the $\text{H-O}_w\text{-H}$ angles between $100\text{--}114^\circ$ and in the O-H distances between $0.89\text{--}1.01 \text{ \AA}$ with the average values 107.8° and $0.956 \text{ \AA}$, in their study of hydrogen bonds in crystalline hydrates. These values, uncorrected for thermal motions, are about 3° larger and $0.02 \text{ \AA}$ shorter than found for a free water molecule at room temperature, for which the mean O-H and $\text{H-O}_w\text{-H}$ values are $0.9743 \text{ \AA}$ and 104.52° .⁹⁴ Pedersen⁹⁵ has calculated that the effect of the vibrational motion for a bonded water molecule will enlarge the angle and shorten the distances in the molecule by about 2° and $0.04 \text{ \AA}$. This implies that, after correction for motion, the O-H distances and the $\text{H-O}_w\text{-H}$ angle in the bonded average water molecule as reported by Ferraris & Franchini-Angela⁸⁷ are stretched $0.02 \text{ \AA}$ and enlarged 1° . In the present study, the deviations from the geometry of the average water molecule are small: the water angle varies from 103.7 to 108.0° and the O-H distances from 0.931 to $0.984 \text{ \AA}$ (Table 4; all values uncorrected for thermal motion). The variation of the donor distances can be explained by the different strengths of the hydrogen bonds. Without exception, longer hydrogen bonds and acceptor distances give shorter O-H bonds. A closer study of the correlation

between acceptor and donor distances of the hydrogen bonds was not performed in this study because only five hydrates were investigated, and no correction for thermal motions has been included in the calculations of the interatomic distances. A correlation study should also take into account the total environment of the water molecule.

Most often both hydrogen atoms of a water molecule are involved in hydrogen bonds, but the coordination on the acceptor side of the oxygen atom can vary considerably. Based on the coordination of the lone-pair orbitals of the water oxygen atom, Chidambaram *et al*⁴⁶ have proposed a classification for crystalline hydrates, which was modified by Hamilton & Ibers,⁹⁷ and further extended by Ferraris & Franchini-Angela.⁸⁷ The water molecules are classified by the number of coordinated cations, the chemical nature of which is indicated by subgroups. Fig. 16 shows a water molecule engaged in two hydrogen bonds $O_w-H\cdots A_{1,2}$ and coordinated to the cations C_1 on

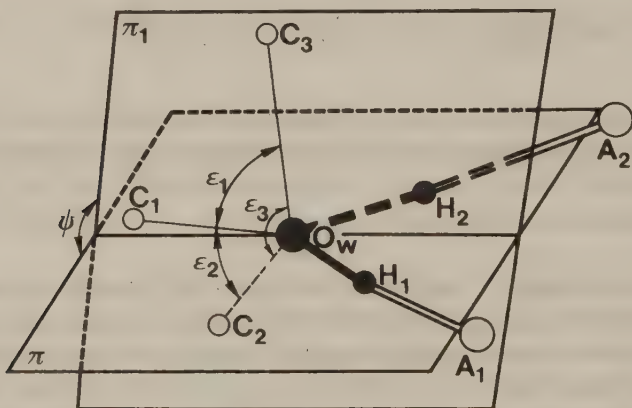


Fig. 16. A water molecule and its environment.

the lone-pair side. The most common coordination types of the water molecule are the tetrahedral and trigonal ones. In the former case, the water molecule is in contact with two acceptors (A_1, A_2) by means of hydrogen bonds, and interacts with two cations or hydrogen bond donors (C_2, C_3) in the directions of the lone pairs. This coordination is most frequent for cations of low charge (M^+, M^{2+}) and hydrogen bond donors. For highly charged cations (M^{3+}, M^{4+}), the most preferred coordination of the water molecule is planar-trigonal, with the cation (C_1) approximately along the bisector of the lone-pair orbitals.

The hydrates studied have all an approximately tetrahedral environment, but it is of course difficult to decide whether this arrangement is due to the influence of the lone pairs or a result of geometrical demands. In order to get an idea of the cation position in relation to the assumed directions of the lone pairs, the angle (ψ) between the plane of the water molecule (π) and the plane (π_1) formed from the atoms O_w , C_2 and C_3 was calculated together with the angles $C_1 \cdots O_w \cdots C_{3,2}$ (ϵ_1, ϵ_2). The point C_1 is situated on the bisector of the lone pairs of the water oxygen atom. In $HgSO_4 \cdot H_2O$ and $HgSeO_4 \cdot H_2O$, the angle between this bisector and the intersectional line of the planes π and π_1 is 5 and 3°, respectively, but for the other hydrates they coincide as a result of the symmetry of the structures. The values in Table 5 indicate that at least for $HgSO_4 \cdot H_2O$ and $HgSeO_4 \cdot H_2O$, where the positions of the atoms C_2 and C_3 are very close to the directions of the lone pairs, the environment of the water molecule is influenced by them and not determined by geometrical requirements alone. For the other three hydrates, the deviations are larger, but the effect of the lone pairs can not be left out of consideration. However, no preference for hydrogen bonds in the directions of the lone pairs was found by Kroon *et al.*⁹⁸ in a statistical analysis of 196 hydrogen bonds in polyalcohols, saccharides and related ROH compounds (45 crystal structures studied by X-ray diffraction).

Table 5. The environment of the water molecules. For definitions of C_1 , ψ and ϵ_i , see Fig. 16. The classification is according to Ferraris & Franchini-Angela⁸⁷

Compound	C_2	C_3	Type	ψ	ϵ_1	ϵ_2	ϵ_3
$HgCrO_4 \cdot \frac{1}{2}H_2O$	Hg	Hg	2B	81.1	43	43	86.3(1)
$HgSO_4 \cdot H_2O$	H	Hg	2H	87.6	50	57	106.7(2)
$Hg_3(OH)_2(SO_4)_2 \cdot H_2O$	Hg	Hg	2B	80.4	70	70	139.9(1)
$HgSeO_4 \cdot H_2O$	Hg	Hg	2B	88.9	54	62	115.7(1)
$HgCl_2 \cdot 2KCl \cdot H_2O$	K	K	2A	89.5	44	44	87.7(1)

V. COMPARISON BETWEEN STRUCTURES OF SALTS OF Hg(II) AND OTHER CATIONS

Structural similarities among salts of group IIB elements

On comparing inorganic structures of the IIB elements (Zn,Cd,Hg), it is obvious that Zn(II) and Cd(II) compounds are more alike than those of Hg(II) and Cd(II). This can seem odd, since for six-coordination the ionic radii⁹⁹ of Cd²⁺ and Hg²⁺, 0.95 and 1.02 Å, are nearly equal and much larger than that of Zn²⁺, 0.74 Å. Compounds of Zn(II) and Cd(II) are often considered to have about the same proportion of ionic character, while those of Hg(II) are appreciably more covalent. On the other hand, both mercury and cadmium compounds are highly toxic, but with different effects, in vivid contrast to zinc, which appears to be an essential micronutrient for all organisms, both plants and animals.

There are only a few compounds of Hg(II) and Zn(II), *e.g.* the sulphides meta-cinnabarite and zinc blende, which crystallize with the same structure. Isomorphous Hg(II) and Cd(II) salts are uncommon, and only for some of them have both structures been investigated. In order to better understand the difference in coordination chemistry of Hg(II) and Cd(II), an investigation of inorganic compounds containing these metals and with the same stoichiometry has been started. Coordination numbers and bond lengths in the isomorphous Cd and Hg structures hitherto investigated by the present author, are given in Table 6. On comparing the selenate

Table 6. Coordination numbers and bond lengths (Å) in some isomorphous Hg and Cd salts

Compound	Coord. number of M	Bond lengths M-O,F	Mean bond length M-O,F	Next nearest neighbours O,F or Cl	Ref.
HgSO ₄	4	2×2.221(6), 2.285(9), 2.420(7)	2.287	2×2.704, 2.772, 2.893	4
CdSO ₄	4	2×2.228(2), 2.233(2), 2.291(2)	2.245	2×2.576, 2.805, 2.922	
HgSeO ₄ ·H ₂ O	6	2.260(1), 2.280(1), 2.332(1) 2.382(1), 2.472(1), 2.499(1)	2.371	2.891	6
CdSeO ₄ ·H ₂ O	6	2.245(2), 2.248(2), 2.271(3) 2.317(3), 2.350(3), 2.420(3)	2.309	2.966	100
HgF(OH)	2	2.10(2), 2.12(2)	2.11 2.40*	2.49[F], 2×2.50[F], 2.69	7
CdF(OH)	6	2.260(5), 2.265(3), 2.272(5) 2.276(5), 2.283(5), 2.283(5)	2.273		101
Hg ₃ O ₂ Cl ₂	2 3+2	2×2.067(14) 2.168(14), 2.323(14), 2.325(14)	2.067 2.272	2×2.918[Cl], 2×2.996[Cl] 2.706[Cl], 2.909[Cl]	9
Cd ₃ O ₂ Cl ₂	2 3+2	2×2.117(3) 2.133(3), 2.219(3), 2.219(3)	2.117 2.190	2×2.741[Cl], 2×2.845[Cl] 2.719[Cl], 2.931[Cl]	102

*Including the six distances Hg-O,F < 2.9 Å.

of Hg(II) and Cd(II), it seems as if the distinction in mean bond length mainly reflects the difference in ionic radius for the metal atoms. The sulphates are irregularly 4-coordinated, but with a tendency for cadmium towards 3+1 and for mercury towards 2+1+1 coordination.

An interesting isomorphous pair is HgF(OH) and CdF(OH) ,¹⁰¹ in which the metal atoms are in contact with six ligands. In HgF(OH) the two bonds, Hg-O , are much shorter than the other four, but in the Cd -compound, where the O and F atoms are statistically distributed, the six Cd-O,F bonds are of the same length, forming an almost regular octahedron around Cd . The structures are of the rutile type, but with the c -axes doubled. The columns of edge-sharing octahedra, parallel to $[001]$, are rotated relative to one another in such a way that an almost perfect hexagonal close-packing of the anions is obtained in CdF(OH) , and a good approximation in HgF(OH) . The difference in packing is probably due to a larger contribution of ionic bonding in CdF(OH) . A similar distortion of the rutile structure, but without the doubling of the c -axis, is found in InO(OH) .¹⁰³ Fig. 17 shows these structures, projected along c . In this projection, the octahedra are superimposed in CdF(OH) and somewhat twisted in HgF(OH) . ZnF_2 ¹⁰⁴ has the rutile structure, while ZnF(OH) ¹⁰⁵ has

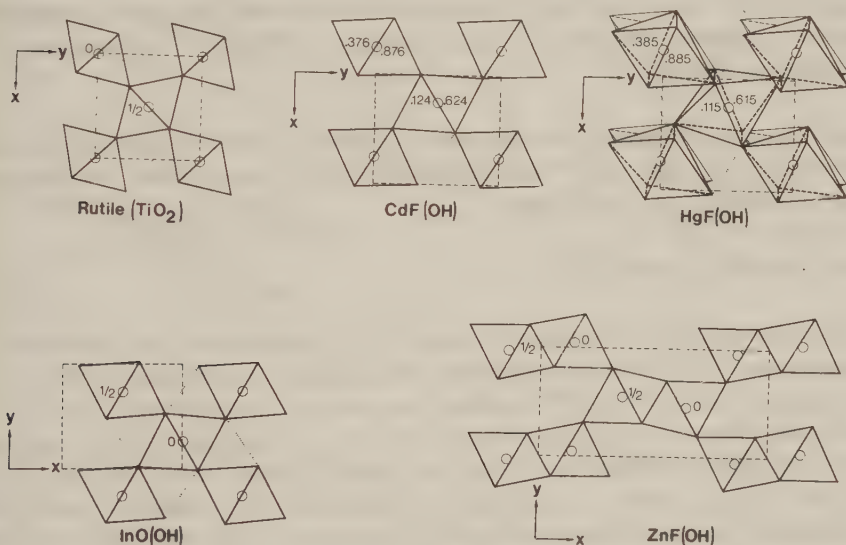


Fig. 17. The structures of TiO_2 , CdF(OH) , HgF(OH) , InO(OH) and ZnF(OH) projected along c . The z -coordinates of the metal atoms are given. The unit cells are indicated with dashed lines, observed hydrogen bonds with dotted.

the diaspore $[\text{AlO}(\text{OH})]$ structure, which is related to the rutile type, but with the columns of octahedra doubled.

In the oxide chlorides, the two independent metal atoms are bonded to 2 and 3+2 ligands in both the Hg and Cd structure (Table 6). The isomorphism is rather surprising, since three-coordination for mercury with oxygen as ligand is unusual, and two-coordination for Cd is very rare. For the linearly coordinated metal atoms, the bonds to Hg are shorter than to Cd. Moreover, the differences between the distances for two-coordination and the shortest for three-coordination are 0.10 for Hg and 0.02 Å for Cd. The same tendency is found for the mean bond lengths for two and three-coordination, which for Hg and Cd deviate with 0.20 and 0.07 Å. This may imply that the two-coordination of Cd is due to geometrical reasons and not to a change in the normal bonding cadmium to oxygen. The structures are stabilized by the arrangement of the oxygen and chlorine atoms, which approximates hexagonal close-packing and the sheets formed from the flattened trigonal pyramids, shown in Fig. 7b, are closer in the Hg-structure, which results in a shorter a -axis.

Other isomorphous inorganic Hg(II) and Cd(II) salts are the fluorides, HgF_2 ⁶⁵ and CdF_2 ^{106,107} with the fluorite structure, in which the metal ion is coordinated by eight fluoride ions. Some ternary fluorides of mercury and cadmium are isomorphous as well *e.g.* HgMnF_6 and CdMnF_6 .⁶⁷ Among chlorides, $\beta\text{-NH}_4\text{HgCl}_3$ ¹⁰⁸ has the same structure as NH_4CdCl_3 .¹⁰⁹

There are also Cd-compounds with the same stoichiometry and most probably with the same structure as $\text{HgF}_2 \cdot 2\text{H}_2\text{O}$ ⁶⁹ and $[\text{Hg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$,⁶² but they have not yet been studied by single-crystal methods.

Other structural relationships

With oxidation number II a filled d-group (d^{10}) is obtained for the IIB subgroup elements, and also for the corresponding isoelectronic ions of group IB (Cu^+ , Ag^+ , Au^+) and III (Ga^{3+} , In^{3+} , Tl^{3+}). Similarities between inorganic structures of Hg(II) and those of the group III metals are rare, but are found for *e.g.* the compounds $\text{HgF}(\text{OH})$ and $\text{InO}(\text{OH})$ (see above). According to Orgel,⁴¹ the formation of colinear bonds by Hg(II) is attributed to a mixing of d and s-orbitals, which can also explain the tendency towards linear coordination of the univalent IB ions.

Two-coordination for Cu(I) is very rare, and observed only with the electronegative O atom in *e.g.* Cu_2O ,¹¹⁰ isomorphous with Ag_2O . Linear coordination is rather common for Ag(I), and is the preferred coordination for Au(I). Of the IB elements the Cu(I) and Ag(I) halides investigated crystallize with the zinc blende, wurtzite

or NaCl-structures, while the Au(I) halides are built up of endless planar zig-zag -X-Au-X- (X = Cl, Br, I) chains with Au linearly coordinated, and with Au-X-Au angles of $92-73^\circ$.^{111,112} A chain of the same type with formula $[\text{HgI}]_n^{n+}$ is formed in $(\text{HgI})_2\text{TiF}_6$,¹¹³ in which the angles at the two independent iodine atoms are 89 and 97° , and the angle at the mercury atom deviates somewhat from linearity (176°). Chains of formula $[\text{HgI}]_n^{n+}$ have also been found in the recently determined structure of HgINO_3 .¹¹⁴ In this compound, the angles at the iodine and mercury atoms are 90 and 159° , respectively, and the structure is closely related to that of the isomorphous compounds Ag_2ClNO_3 ¹¹⁵ and Ag_2BrNO_3 .¹¹⁶ In the latter structures, one of the two independent silver atoms replaces the Hg atom in the $[\text{HgI}]_n^{n+}$ chain and the other silver atom is in a position not occupied in the HgINO_3 structure.

Sometimes small changes in the positional parameters alter the description of the building elements of a structure, as found in the isomorphous compounds HgCrO_4 and AgMnO_4 .¹¹⁷ The coordination polyhedra are distorted pentagonal bipyramids in both structures (Fig. 18), but in HgCrO_4 two of the Hg-O bonds are much shorter than the others and the structure is best described by infinite $[\text{HgCrO}_4]_n$ zig-zag chains (Fig. 2a). The two short Hg-O bonds in HgCrO_4 are accompanied by an elongation of the corresponding Cr-O bonds, which results in a more deformed tetrahedron around Cr than around Mn in AgMnO_4 .

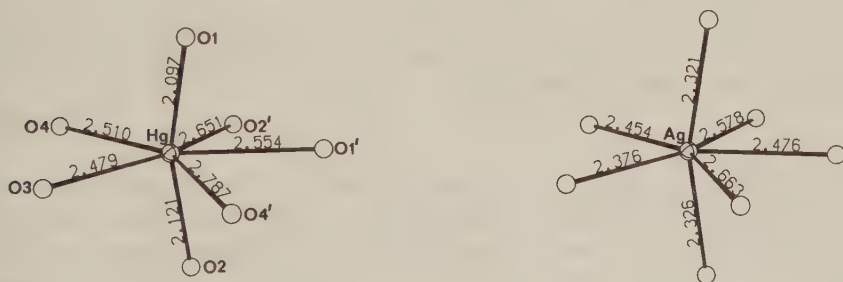


Fig. 18. The coordination around Hg and Ag in the structures of HgCrO_4 and AgMnO_4 .

Another example of two compounds which crystallize in the same space group and with almost the same atomic coordinates, but with different coordination about the metal atoms, are AgF_2 ¹¹⁸ and $\beta\text{-HgO}_2$.⁴⁸ In both compounds, the metal atoms are surrounded by six ligands forming distorted octahedra. In $\beta\text{-HgO}_2$, Hg is coordinated by two short bonds [2.06 Å] and four longer ones [2.67 Å], and normally the compound is described as built up of -Hg-O-O-Hg- chains formed from the short bonds. In AgF_2 ,

on the other hand, Ag has a square-planar configuration with four Ag-F bonds of 2.07 Å and with two next nearest fluorine atoms at 2.58 Å. Considering only the shorter bonds, this structure is composed of layers.

Structural similarities exist between compounds of Hg(II) and Au(I). There are also similarities between compounds of Hg(II) and Ag(I), even if, as shown by Werner & Strähle,¹¹⁹ silver has a more ionic character and higher coordination numbers than monovalent gold, which prefers linear coordination and covalent bonds.

VI. SUMMARY

The coordination of Hg(II) in inorganic compounds with Hg-O, Hg-F and Hg-Cl bonds has been studied by X-ray and neutron diffraction methods. The roles of the water molecules and the hydrogen bonds in the structures of the hydrates investigated are discussed. Structural relationships between salts of Hg(II) and salts of other cations have also been studied, especially Cd(II) with the same stoichiometry.

The tendency to form two short linear or almost linear bonds is pronounced for Hg(II), and is found among the cations of other elements mainly for Au(I). In many mercury(II) structures, this disposition leads to chains of different geometries as building elements. Such chains, originally discovered in mercury(II) oxide, are shown to exist in *e.g.* the mercury chromates HgCrO_4 and $\text{HgCrO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. Endless chains of formula $[\text{Hg}(\text{OH})]_n^{n+}$ are found in $\text{HgF}(\text{OH})$, and a finite chain exists in $\text{Hg}_3(\text{OH})_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. The chains can also be further linked, as in $\text{Hg}_6\text{O}_4\text{Cl}_4$, or condensed to layers, as in $\text{Hg}_3\text{O}_2\text{CrO}_4$. Discrete mononuclear molecules with digonally coordinated mercury(II) are found in $\text{HgSO}_4 \cdot \text{H}_2\text{O}$ and $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$. The linear two-coordination is in most of the structures extended by three to five weaker bonds to ligands at distances shorter than the sum of the van der Waals radii.

Coordination numbers three and four are unusual for Hg when oxygen is the ligand, but are found in $\text{Hg}_3\text{O}_2\text{Cl}_2$ and HgSO_4 ; with chlorine as a ligand, three-coordination is fairly common. Five-coordination of oxygen to mercury has not yet been observed, but it exists for chlorine. The polyhedron around the metal atoms is then a trigonal bipyramid.

Six-coordinated Hg(II) was first found in $[\text{Hg}(\text{C}_6\text{H}_5\text{NO})_6](\text{ClO}_4)_2$, published in 1973, and has since then been observed in a few compounds, for example $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$. A coordination number higher than six for Hg-O coordination has until now only been reported for $\text{K}_3[\text{Hg}(\text{NO}_2)_4]\text{NO}_3$, but in this work it is shown also to exist in two mercury(II) bromates.

Neutron diffraction studies have been carried out on five crystalline mercury(II) hydrates. The water molecules in these structures play an important role in linking structural elements by hydrogen bonds, which are weak or of intermediate strength. The water molecules are thus essential for the formation of the structures and the hydrates can not be dehydrated without destruction, which is obvious from DTA and subsequent X-ray powder investigations. The environments of the water molecules are tetrahedral, and in most cases Hg(II) atoms are approximately in the directions of the lone pairs.

Endless zig-zag chains, of the same type as those found in Hg(II) salts, are also present in the compounds AuCl, AuBr and AuI. Only a few Au(I) compounds have been prepared, since Au(I) disproportionates in aqueous solutions, and a closer comparison between structures of Hg(II) and Au(I) is therefore not possible.

Similarities between structures of two or three-coordinated Hg(II) and Cd(II) are very rare. However, the structures of $\text{Hg}_3\text{O}_2\text{Cl}_2$ and $\text{Cd}_3\text{O}_2\text{Cl}_2$ are isomorphous, with digonal and trigonal coordination for the two independent metal atoms. With higher coordination numbers, structural relationships between salts of Hg(II) and Cd(II) are less unusual, and are found *e.g.* for four-coordination in the sulphates HgSO_4 and CdSO_4 , and for six-coordination in the selenates $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$ and $\text{CdSeO}_4 \cdot \text{H}_2\text{O}$. In isomorphous Hg(II) and Cd(II) structures, the more pronounced covalent character of Hg(II) leads to differences in the positions of the metal and/or the ligands atoms to give a distortion towards two-coordination.

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